

Supplementary Materials

Chemical Constituents from Leaves of *Baccharis sphenophylla* (Asteraceae) and Their Antioxidant Effects

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NMR data for characterization of the isolated compounds

ent-Kaurenoic acid (1): ¹H NMR (300 MHz, CDCl₃) δ_H: 0.80 (1H, m, H-1), 1.9-1.8 (4H, m, H-1, H-2, H-6), 1.6-1.4 (7H, m, H-2, H-7, H-11, H-12), 1.03 (1H, m, H-3), 2.15 (1H, m, H-3), 1.2-1.1 (3H, m, H-5, H-9, H-14), 2.65 (1H, sl, H-13), 2.00 (1H, m, H-14), 2.19 (2H, s, H-15), 4.81 (1H, sl, H-17), 4.76 (1H, sl, H-17), 0.97 (3H, s, H-18), 1.27 (3H, s, H-20). ¹³C NMR (75.5 MHz, CDCl₃) δ_C: 40.7 (C-1), 19.1 (C-2), 37.8 (C-3), 43.7 (C-4), 57.0 (C-5), 21.8 (C-6), 41.3 (C-7), 44.2 (C-8), 55.1 (C-9), 39.6 (C-10), 18.4 (C-11), 33.1 (C-12), 43.8 (C-13), 39.7 (C-14), 49.0 (C-15), 155.9 (C-16), 103.0 (C-17), 29.0 (C-18), 183.8 (C-19), 15.6 (C-20).

Hispidulin (2): ¹H NMR (300 MHz, DMSO-d₆) δ_H: 6.73 (1H, s, H-3), 6.58 (1H, s, H-8), 7.89 (2H, d, *J* = 8.8 Hz, H-2', H-6'), 6.92 (2H, d, *J* = 8.8 Hz, H-3', H-5'), 3.75 (3H, s, OCH₃), 13.05 (s, OH-C₅). ¹³C NMR (75.5 MHz, DMSO-d₆) δ_C: 164.3 (C-2), 102.8 (C-3), 182.5 (C-4), 153.2 (C-5), 131.7 (C-6), 157.7 (C-7), 94.7 (C-8), 152.8 (C-9), 104.4 (C-10), 121.6 (C-1'), 128.9 (C-2', C-6'), 116.4 (C-3', C-5'), 161.7 (C-4'), 60.6 (OCH₃).

Eupafolin (3): ¹H NMR (300 MHz, DMSO-d₆) δ_H: 6.66 (s, H-3), 6.58 (s, H-8), 7.40 (1H, d, *J* = 2.0 Hz, H-2'), 6.89 (1H, d, *J* = 8.0 Hz, H-5'), 7.42 (1H, dd, *J* = 8.0 and 2.0 Hz, H-6'), 3.75 (3H, s, OCH₃), 13.09 (s, OH-C₅). ¹³C NMR (75.5 MHz, DMSO-d₆) δ_C: 164.2 (C-2), 102.9 (C-3), 182.3 (C-4), 153.1 (C-5), 131.8 (C-6), 158.3 (C-7), 94.5 (C-8), 152.8 (C-9), 104.2 (C-10), 121.8 (C-1'), 113.6 (C-2'), 146.2 (C-3'), 150.2 (C-4'), 116.4 (C-5'), 119.2 (C-6'), 60.3 (OCH₃).

5-*O*-Caffeoylquinic acid (4): ¹H NMR (300 MHz, CD₃OD) δ_H: 1.90-2.10 (4H, m, H-2, H-6), 5.17 (1H, m, H-3), 3.70 (1H, dd, *J* = 3.3, 7.5 Hz, H-4), 4.08 (1H, dd, *J* = 3.2, 6.9 Hz, H-5), 7.13 (d, *J* = 1.8 Hz, H-2'), 6.84 (d, *J* = 8.4 Hz, H-5'), 7.03 (dd, *J* = 1.8, 8.4 Hz, H-6'), 7.58 (d, *J* = 16.0 Hz, H-7'), 6.34 (d, *J* = 16.0 Hz, H-8'). ¹³C NMR (75.5 MHz, CD₃OD) δ_C: 73.5 (C-1), 37.4 (C-2), 72.5 (C-3), 72.9 (C-4), 70.1 (C-5), 38.6 (C-6), 176.3 (C-7), 127.6 (C-1'), 115.4 (C-2'), 147.1 (C-3'), 149.7 (C-4'), 116.9 (C-5'), 123.3 (C-6'), 147.5 (C-7'), 115.5 (C-8'), 168.5 (C-9').

5-*O*-Caffeoylquinic acid methyl ester (5): ¹H NMR (CD₃OD, 300 MHz) δ: 1.91-2.08 (4H, m, H-2, H-6), 5.18 (1H, m, H-3), 3.63 (1H, dd, *J* = 3.1, 7.4 Hz, H-4), 4.04 (1H, dd, *J* = 3.3, 6.7 Hz, H-5), 7.06 (1H, d, *J* = 1.9 Hz, H-2'), 6.80 (1H, d, *J* = 8.1 Hz, H-5'), 6.97 (1H, dd, *J* = 1.9, 8.1 Hz, H-6'), 7.55 (1H, d, *J* = 15.9 Hz, H-7'), 6.24 (1H, d, *J* = 15.9 Hz, H-8'); 3.60 (3H, s, COOCH₃); ¹³C NMR (CD₃OD, 75.5 MHz) δ_C: 75.9 (C-1), 37.9 (C-2), 72.3 (C-3), 72.6 (C-4), 70.4 (C-5), 38.2 (C-6), 175.6 (C-7), 127.8 (C-1'), 115.2 (C-2'), 147.0 (C-3'), 149.9 (C-4'), 116.7 (C-5'), 123.0 (C-6'), 147.4 (C-7'), 115.3 (C-8'), 168.4 (C-9'), 53.1 (OCH₃).

3,4-di-*O*-Caffeoylquinic acid (6): ¹H NMR (300 MHz, CD₃OD) δ_H: 2.12 (2H, m, H-2), 5.64 (m, H-3), 5.12 (dd, *J* = 2.9, 9.1 Hz, H-4), 4.37 (sl, H-5), 2.27 (2H, m, H-6), 7.01 / 7.02 (d, *J* = 2.0 Hz, H-2' / H-2''), 6.74 / 6.75 (d, *J* = 8.2 Hz, H-5' / H-5''), 6.90 / 6.92 (dd, *J* = 2.0, 8.2 Hz, H-6' / H-6''), 7.52 / 7.60 (d, *J* = 15.9 Hz, H-7' / H-7''), 6.19 / 6.29 (d, *J* = 15.9 Hz, H-8' / H-8''). ¹³C NMR (75.5 MHz, CD₃OD) δ_C: 76.0 (C-1), 39.6 (C-2), 69.2 (C-3), 76.0 (C-4), 69.7 (C-5), 38.5 (C-6), 176.0 (C-7), 127.7 (C-1'), 115.3 (C-2'), 146.9 (C-3'), 149.8 (C-4'), 123.3 (C-5'), 116.6 (C-6'), 147.7 (C-7'), 115.3 (C-8'), 168.7 (C-9'), 127.8 (C-1''), 114.9 (C-2''), 146.9 (C-3''), 149.8 (C-4''), 123.3 (C-5''), 116.6 (C-6''), 147.8 (C-7''), 114.8 (C-8''), 168.4 (C-9'').

3,5-di-O-Caffeoylquinic acid (**7**): ^1H NMR (300 MHz, CD_3OD) δ_{H} : 2.20 (2H, m, H-2), 5.38 (m, H-3), 3.97 (dd, J = 3.2, 7.8 Hz, H-4), 5.42 (sl, H-5), 2.34 (2H, sl, H-6), 7.07 (2H, sl, H-2', H-2''), 6.78 (2H, d, J = 8.2 Hz, H-5', H-5''), 6.97 (2H, dl, J = 8.2 Hz, H-6', H-6''), 7.58 / 7.61 (d, J = 15.9 Hz, H-7' / H-7''), 6.27 / 6.36 (d, J = 15.9 Hz, H-8' / H-8''). ^{13}C NMR (75.5 MHz, CD_3OD) δ_{C} : 74.7 (C-1), 38.2 (C-2), 72.2 (C-3), 71.0 (C-4), 72.8 (C-5), 36.1 (C-6), 177.7 (C-7), 127.8 (C-1'), 115.3 (C-2'), 146.8 (C-3'), 149.6 (C-4'), 123.1 (C-5'), 116.5 (C-6'), 147.1 (C-7'), 115.7 (C-8'), 169.0 (C-9'), 128.0 (C-1''), 115.2 (C-2''), 146.5 (C-3''), 149.5 (C-4''), 123.0 (C-5''), 116.5 (C-6''), 147.3 (C-7''), 115.2 (C-8''), 168.4 (C-9'').

4,5-di-O-Caffeoylquinic acid (**8**): ^1H NMR (300 MHz, CD_3OD) δ_{H} : 2.12 (m, H-2 / H-6), 2.20 (sl, H-2), 4.36 (m, H-3), 5.01 (dd, J = 3.2, 8.8 Hz, H-4), 5.64 (sl, H-5), 2.37 (sl, H-6), 7.02 / 7.04 (d, J = 1.8 Hz, H-2' / H-2''), 6.73 / 6.77 (d, J = 8.2 Hz, H-5' / H-5''), 6.88 / 6.91 (dd, J = 1.8, 8.2 Hz, H-6' / H-6''), 7.55 / 7.57 (d, J = 15.9 Hz, H-7' / H-7''), 6.26 / 6.28 (d, J = 15.9 Hz, H-8' / H-8''). ^{13}C NMR (75.5 MHz, CD_3OD) δ_{C} : 76.6 (C-1), 41.9 (C-2), 65.9 (C-3), 75.2 (C-4), 70.3 (C-5), 37.0 (C-6), 178.2 (C-7), 127.9 (C-1'), 115.2 (C-2'), 146.9 (C-3'), 149.8 (C-4'), 123.3 (C-5'), 116.6 (C-6'), 147.2 (C-7'), 115.3 (C-8'), 168.8 (C-9'), 127.8 (C-1''), 115.1 (C-2''), 146.9 (C-3''), 149.8 (C-4''), 123.1 (C-5''), 116.5 (C-6''), 146.2 (C-7''), 115.0 (C-8''), 168.7 (C-9'').

3,5-di-O-Caffeoylquinic acid methyl ester (**9**): ^1H NMR (300 MHz, CD_3OD) δ_{H} : 2.16 (2H, m, H-2), 5.30 (m, H-3), 3.98 (dd, J = 3.2, 6.5 Hz, H-4), 5.40 (m, H-5), 2.32 (2H, m, H-6), 7.06 / 7.07 (d, J = 1.9 Hz, H-2' / H-2''), 6.78 / 6.79 (d, J = 8.2 Hz, H-5' / H-5''), 6.97 (2H, dd, J = 1.8, 8.2 Hz, H-6', H-6''), 7.55 / 7.62 (d, J = 15.9 Hz, H-7' / H-7''), 6.22 / 6.34 (d, J = 15.9 Hz, H-8' / H-8''), 3.69 (3H, s, OCH_3). ^{13}C NMR (75.5 MHz, CD_3OD) δ_{C} : 74.5 (C-1), 35.5 (C-2), 71.8 (C-3), 69.6 (C-4), 72.1 (C-5), 36.5 (C-6), 175.5 (C-7), 127.7 (C-1'), 114.7 (C-2'), 146.7 (C-3'), 149.4 (C-4'), 116.4 (C-5'), 123.9 (C-6'), 147.0 (C-7'), 114.9 (C-8'), 167.8 (C-9'), 127.5 (C-1''), 114.9 (C-2''), 146.6 (C-3''), 149.6 (C-4''), 116.5 (C-5''), 123.9 (C-6''), 147.7 (C-7''), 115.3 (C-8''), 168.6 (C-9''), 52.9 (OCH_3).

Caffeic acid (**10**): this compound was identified through co-injection of the commercial standard of the sample.

Quercetin 3-O- β -glucopyranoside (**11**): ^1H NMR (300 MHz, DMSO-d_6) δ_{H} : 6.17 (1H, sl, H-6), 6.37 (1H, sl, H-8), 7.57 (1H, d, J = 2.1 Hz, H-2'), 6.82 (1H, d, J = 9.0 Hz, H-5'), 7.57 (1H, dd, J = 2.1, 9.0 Hz, H-6'), 5.45 (1H, d, J = 7.3 Hz, H-1''), 3.90 – 3.00 (4H, m, H-2'' to H-5''), 3.56 (2H, d, J = 11.5 Hz, H-6''); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ_{C} : 156.9 (C-2), 133.9 (C-3), 177.9 (C-4), 161.7 (C-5), 99.4 (C-6), 165.2 (C-7), 94.2 (C-8), 156.7 (C-9), 104.1 (C-10), 122.3 (C-1'), 115.8 (C-2'), 145.5 (C-3'), 148.7 (C-4'), 116.5 (C-5'), 121.7 (C-6'), 101.5 (C-1''), 74.5 (C-2''), 77.0 (C-3''), 70.4 (C-4''), 78.1 (C-5''), 61.5 (C-6'').

Quercetin 3-O- α -rhamnopyranoside (**12**): ^1H NMR (300 MHz, DMSO-d_6) δ_{H} : 6.16 (1H, sl, H-6), 6.35 (1H, sl, H-8), 7.55 (1H, d, J = 2.1 Hz, H-2'), 6.82 (1H, d, J = 9.0 Hz, H-5'), 7.55 (1H, dd, J = 2.1, 9.0 Hz, H-6'), 5.32 (1H, d, J = 7.3 Hz, H-1''), 3.90 – 3.00 (4H, m, H-2'' to H-5''), 0.91 (3H, d, J = 5.6 Hz, H-6''); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ_{C} : 158.1 (C-2), 134.9 (C-3), 177.9 (C-4), 163.1 (C-5), 99.5 (C-6), 166.0 (C-7), 94.5 (C-8), 159.1 (C-9), 105.6 (C-10), 123.3 (C-1'), 116.4 (C-2'), 145.7 (C-3'), 149.5 (C-4'), 117.7 (C-5'), 123.0 (C-6'), 102.5 (C-1''), 71.4 (C-2''), 70.9 (C-3''), 71.5 (C-4''), 68.5 (C-5''), 18.2 (C-6'').

Quercetin 3-O- β -(6''-O- α -rhamnosyl)-glucopyranoside (**13**): ^1H NMR (300 MHz, DMSO-d_6) δ_{H} : 6.17 (1H, sl, H-6), 6.35 (1H, sl, H-8), 7.53 (1H, d, J = 2.1 Hz, H-2'), 6.82 (1H, d, J = 9.0 Hz, H-5'), 7.54 (1H, dd, J = 2.1, 9.0 Hz, H-6'), 5.33 (1H, d, J = 7.2 Hz, H-1''), 3.90 – 3.00 (6H, m, H-2'' to H-6''), 4.35 (1H, sl, H-1'''), 3.90 – 3.00 (4H, m, H-2''' to H-5'''), 0.98 (3H, d, J = 6.1 Hz, H-6'''); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ_{C} : 157.2 (C-2), 134.1 (C-3), 177.9 (C-4), 161.6 (C-5), 99.5 (C-6), 165.6 (C-7), 94.4 (C-8), 156.9 (C-9), 104.4 (C-10), 121.9 (C-1'), 115.9 (C-2'), 145.5 (C-3'), 149.7 (C-4'), 116.8 (C-5'), 121.5 (C-6'), 101.6 (C-1''), 74.6 (C-2''), 76.2 (C-3''), 70.5 (C-4''), 76.9 (C-5''), 67.7 (C-6''), 101.4 (C-1'''), 71.2 (C-2'''), 70.7 (C-3'''), 71.7 (C-4'''), 68.5 (C-5'''), 18.4 (C-6'').

Kaempferol-3-O- β -(6''-O- α -rhamnosyl)-galactopyranoside (**14**): ^1H NMR (300 MHz, DMSO-d_6) δ_{H} : 6.10 (1H, d, J = 1.6 Hz, H-6), 6.31 (1H, d, J = 1.6 Hz, H-8), 8.01 (2H, d, J = 8.9 Hz, H-2', H-6'), 6.85 (2H, d, J = 8.9 Hz, H-

3', H-5'), 5.21 (1H, d, J = 7.6 Hz, H-1''), 4.39 (1H, sl, H-1'''), 3.90-3.00 (10H, m, H-2'' to H-6'', and H-2''' to H-5'''), 1.04 (3H, d, J = 6.2 Hz, H-6'''). ^{13}C NMR (75.5 MHz, DMSO- d_6) δ_{C} : 156.8 (C-2), 133.8 (C-3), 177.6 (C-4), 161.5 (C-5), 100.2 (C-6), 168.5 (C-7), 94.7 (C-8), 157.2 (C-9), 103.0 (C-10), 121.5 (C-1'), 131.4 (C-2', C-6'), 115.3 (C-3', C-5'), 160.5 (C-4'), 103.5 (C-1''), 71.6 (C-2''), 73.5 (C-3''), 68.5 (C-4''), 74.2 (C-5''), 66.3 (C-6''), 100.2 (C-1'''), 70.8 (C-2'''), 71.1 (C-3'''), 72.5 (C-4'''), 68.9 (C-5'''), 18.1 (C-6''').

6,8-di-C- β -Glucopyranosyl-apigenin (**15**): ^1H NMR (300 MHz, DMSO- d_6) δ_{H} : 6.90 (1H, s, H-3), 8.08 (2H, d, J = 8.5 Hz, H-2', H-6'), 6.93 (2H, d, J = 8.5 Hz, H-3', H-5'), 4.91 (1H, d, J = 10.1 Hz, H-1''), 4.76 (1H, d, J = 10.1 Hz, H-1'''), 3.90-3.20 (12H, m, H-2''-H-6'', and H-2'''-H-6'''). ^{13}C NMR (75.5 MHz, DMSO- d_6) δ_{C} : 164.6 (C-2), 103.2 (C-3), 182.9 (C-4), 159.3 (C-5), 108.3 (C-6), 161.9 (C-7), 106.0 (C-8), 155.8 (C-9), 103.1 (C-10), 122.2 (C-1'), 129.7 (C-2', C-6'), 116.5 (C-3', C-5'), 161.9 (C-4'), 72.6 (C-1''), 71.7 (C-2''), 79.6 (C-3''), 69.8 (C-4''), 82.6 (C-5''), 60.6 (C-6''), 74.8 (C-1'''), 71.3 (C-2'''), 79.6 (C-3'''), 69.8 (C-4'''), 81.6 (C-5'''), 62.0 (C-6''').